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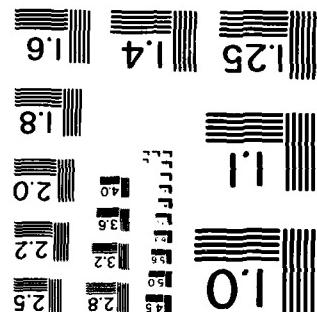
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Fluctuation Phenomena Studies in Chemically Sensitive Field Effect Transistors Part II. Corrosion of Silicon Oxynitride		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) Zheng Kang Li, J. M. Reijn and J. Janata		6. PERFORMING ORG. REPORT NUMBER
9. FUNDING ORGANIZATION NAME AND ADDRESS Department of Bioengineering University of Utah Salt Lake City, Utah 84221		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-77815-79-81(472)
11. CONTROLLING OFFICE NAME AND ADDRESS S. Max Irving, Office of Naval Research University of New Mexico, Room 204, Bandolier Hall West, Albuquerque, New Mexico 87131		12. REPORT DATE November 20, 1984
13. NUMBER OF PAGES		14. SECURITY CLASS. (If this report) unclassified
		15. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) ed for public release: distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 30, if different from Report)		
18. FINGERPRINT NOTES Accepted for publication in J. Electrochem. Soc.		
19. ABSTRACT (Continue on reverse side if necessary and identify by block number) Chemically Sensitive Field Effect Transistor: Fluctuation Analysis; Corrosion of Insulators; Silicon Oxynitride		
20. BODY TEXT (Continue on reverse side if necessary and identify by block number) Drain current fluctuations in a field effect transistor caused by the corrosion of silicon oxynitride have been measured and analyzed. It has been shown that under wet etching conditions the surface of silicon oxynitride becomes conducting. The equivalent electrical circuit corresponding to this situation has been proposed.		

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FLUCTUATION PHENOMENA STUDIES

IN CHEMICALLY SENSITIVE FIELD EFFECT TRANSISTORS

PART II. CORROSION OF SILICON OXYNITRIDE

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Submitted to J. Electrochem. Soc.
 Descriptors: Insulator; Etching; Integrated Circuits; Surfaces

DISTRIBUTION STATEMENT A	
Approved for public release; Distribution Unlimited	

ABSTRACT

Drain current fluctuations in a field effect transistor caused by the corrosion of silicon oxynitride have been measured and analyzed. It has been shown that under wet etching conditions the surface of silicon oxynitride becomes conducting. The equivalent electrical circuit corresponding to this situation has been proposed.

INTRODUCTION

Analysis of equilibrium [1] and non-equilibrium noise [2] in CHEMFETs has shown that electrochemical information can be obtained from the solution/membrane [1] or solution/metal [2] interface without external electrical perturbation. The system is "allowed to tell its own story", so to speak. The unique feature of CHEMFET lies in the fact that the electrochemical signal is coupled through the electric field directly to the transistor channel. In other words, there is no need for connecting the interface under study to the amplifier through a metal lead which would introduce a parasitic impedance into the measurement. Under these conditions any material, conductor, semiconductor or insulator, deposited directly over the gate of the CHEMFET can be studied by this technique. In this paper we will describe study of electrochemical processes which are taking place at the surface of the gate insulator during a wet etching reaction. The theoretical background for this work has been outlined in Part I of this series.

EXPERIMENTAL

Transistors used in this study were of the same type as used previously [2] except for the aluminum layer (Part I, Fig. 1) which was not present. The size of the gates was $20 \times 400 \mu\text{m}$ and they were spaced $700 \mu\text{m}$ apart. The area of the chip exposed to the etching solution was typically $0.9 - 1.0 \text{ mm}^2$. A slightly different instrumentation approach has been used. The outputs from the two preamplifiers (PARC 113A) are connected to the signal analyzer HP 3582A (Hewlett Packard) and also to a digitizing oscilloscope (Tektronix 5225). Signals were recorded on an FM tape recorder (Hewlett Packard model 3964A). This arrangement allows for on line spectral analysis using the spectrum analyzer and for off line analysis using our computer system.

The computer system used is an LSI 11/23 based minicomputer (Digital Equipment) running under an RT-11 5.1 operating system. Storage facilities are a 10 megabyte RL01 hard disk (Digital Equipment) and a dual RX02 floppy disk system (Data Systems Design) mainly used for backup purposes. Standard programming language is FORTRAN IV version 2.6 (Digital Equipment). We developed a Ratfor preprocessor to extend this language [3].

The computer performs a variety of tasks:

-data acquisition:

A Tektronix 5223 digitizing oscilloscope is connected through an HP-IB instrument interface bus. This arrangement allows for acquisition of two channel time records of 1016 points each, digitized to 10 bits including sign. During the time needed for data transfer the sampling is interrupted and thus a discontinuous time series is obtained. As pointed out in the previous paper this can be allowed for if the stochastic process is stationary and ergodic. For the non-stationary cases we are studying alternatives to obtain continuous time series.

-data qualification:

Software is available to inspect time records for stationarity. The main test performs a fit of experimental data to a Gaussian PDF. This test enables to distinguish between 'true' signals and unwanted disturbances. Furthermore, spectral analysis of non-stationary data yields results which have to be regarded very critically with respect to their interpretation. Use of the spectrum analyzer yields only averaged spectral estimates and, therefore, information is lost in this computation. Even if the experimental data are expected to be stationary (for instance in equilibrium noise measurements) it is good practice to subject (part of) the time history of the experiment to statistical tests [4].

-data processing:

Programs are available for spectral analysis yielding estimates of the auto and cross spectral densities and the coherence function. In the time domain auto and cross correlations can be calculated for individual time records.

-data presentation:

The software supports a HP 7220C digital plotter (Hewlett Packard) for permanent copies of graphs and a graphical terminal MG3000 (Wicat) for quick visualization of results.

-data modelling:

The main programs in this group perform curve fitting as mentioned above for the PDF. The software is adapted from Bevington [5] and is written using the Marquardt algorithm.

Copies of programs are available upon request.

Solutions used in this study were 0.1 M pH 7.00 phosphate buffer and etching solution containing 100 ml 85% w/w H_3PO_4 , A.C.S. Certified, Fisher and 5 ml 48-50% w/w HBF_4 , Purified, Fisher. Solutions were handled using the same manifold as described in Part I.

RESULTS

The time record of the noise in buffer solution (equilibrium) and at 55°C in the etching solution (corrosion) are shown in Fig. 1. The temperature for etching of silicon oxynitride under normal processing conditions is 180°C . At that temperature silicon oxynitride is removed at the rate of $\sim 50 \text{ \AA min.}^{-1}$. We have found that the highest temperature under which our noise measurements could be done reproducibly was 55°C . At higher temperatures the overall fluctuations were too violent, and samples were destroyed too quickly. The autospectral density of corroding silicon oxynitride was found to be strongly dependent on temperature, (Fig. 2a) and on mass transport (Fig. 3a).

The most surprising result of this work has been the strong correlation between signals from the gate A and the gate B (Fig. 1, Part I) during corrosion conditions. As a matter of fact, the cross power spectral density and auto power spectral density calculated for the same corroding sample are almost identical. Consequently, the coherence function, γ^2 , (Part I) has a non-zero value over broad range of frequencies meaning that there is a strong correlation between these two signals. Thus, coherence is again strongly dependent on temperature (Fig. 2b), and on flow-rate (Fig. 3b). The data in Figures 2 and 3 are presented on different frequency scales in order to highlight the shapes of these frequency dependent functions.

It has been found that the coherence function measured under mildest etching corrosion conditions ($30\text{--}38^{\circ}\text{C}$) slowly shifts towards lower frequencies with time. At temperatures above 45°C such shifts have not been observed. The time-dependent surface conductivity has been suspected to be the cause of this behavior. In order to verify this hypothesis, the following experimental sequence has been tried. The sample was first placed in the

etching solution at 25^oC. Under those conditions no coherence occurs in the frequency range accessible to our measurements (0.8Hz - 25kHz) (Fig. 4, curve 1). Without interrupting the flow of the etching solution, the heater was turned on and the temperature of the etching solution was raised to 38^oC (Fig. 4, Curve 2). After 4 minutes the coherence has decreased gradually (Fig. 4, curve 3). The heater was then disconnected for four minutes and the coherence at 25^oC was again measured; it had returned to near zero value. After 4 minutes the temperature was again raised to 38^oC. The coherence function has reached lower value than that obtained during the first cycle (Fig 4, curve 4) and again gradually decreased with time. This behavior is consistent with formation (25^oC) and removal (38^oC) of surface conductive layer which is necessary for the non-zero value of the coherence function. It must be pointed out that zero value of coherence at 25^oC does not imply the absence of surface conductive layer. It can mean the absence of the common correlated source of fluctuation i.e., the corrosion process, or it can mean that the surface resistance is so high that the coherence is shifted to frequencies below 0.8Hz.

DISCUSSION

There are two significant results of this study: the ability to investigate directly the electrochemical corrosion process which is taking place at the insulator/solution interface and the finding that the entire surface of the silicon oxynitride becomes conductive during wet etching. The latter result, unfortunately, makes the interpretation of the fluctuation phenomena difficult, at present. The time record of the corrosion process (Fig. 1) reflects the nature of the physical process itself. Each current excursion corresponds to an instantaneous charge imbalance at the gate capacitor. This can be due to random interaction of ions (both positive and negative) with the silicon oxynitride surface, ion exchange, or physical removal of charged material from the surface (etching). Any or all of these processes take place at the entire surface of the transistor chip. The original hypothesis has been that only the interactions taking place directly over the gate area A and B would be contributing to the fluctuations in those respective channels and be uncorrelated. This situation is in direct contrast to the experimental conditions for the corrosion study of aluminum (Part I) in which the electrochemically generated fluctuations were made intentionally correlated to both gates through a common, metallic connection.

The presence of strongly correlated fluctuation source in the case of silicon oxynitride points to the existence of a conducting layer which is spread over the entire silicon oxynitride surface. Since this surface is laterally homogeneous chemically, it is reasonable to expect that the corrosion and hence the source of fluctuations is distributed uniformly over the entire surface. The process can be, therefore, modeled as a distributed impedance as shown in Fig. 5a. In this model the whole surface of the chip is subdivided into elementary complex impedance cells (Fig. 5b). In the first

approximation it is assumed that the conduction takes place in a two-dimensional conducting plane array of the elements Z_{jk} . It is further assumed that the elementary fluctuation sources, S_{jk} are connected to the center of each impedance element Z_{jk} (Fig. 5b) and that the interconnections between neighboring elements are only orthogonal. Through this two-dimensional network each noise source anywhere on the chip surface contributes to the fluctuations measured in channels A and B.

The experiment described in Fig. 4 allows us to speculate about the nature of the plane conductor. At high temperature ($> 45^{\circ}\text{C}$) the coherence function has a non-zero value which does not decrease in time. This means that the surface conductor is being formed continuously. At 38°C the auto spectral density is high, meaning that the corrosion related fluctuation source is operative but the coherence function gradually shifts to lower frequencies (Fig. 4, curves 2, 4, 5). This is consistent with the increase of the resistance value in the impedance element (Fig. 5b) which would effectively filter out the higher frequencies of the coherence function.

Periods 1, 3 and 6 in Fig. 4 represent time intervals in which the surface conductor can re-form. High values of the coherence function in the intervals 2, 4 and 5 support this hypothesis.

So far, we have been considering only a two-dimensional planar conductor which is formed chemically. There is other evidence which suggests that this conductor is a three dimensional layer of finite thickness. In that sense the observed changes in the resistance as inferred from the time dependence of the coherence function can be due to the changes in the geometry of the layer (thickness) and/or of the volume density of charge carriers in that layer. At present, this question cannot be resolved on the basis of experimental evidence available to us.

The other supporting argument for the existence of the active surface layer comes from the analysis of concentration profiles of silicon oxynitride which has been done by both Auger spectroscopy [6,7] and by ESCA [8] combined with argon ion sputtering. An oxygen rich layer approximately 50 Å thick has been found to exist on the surface of silicon nitride. This layer re-forms spontaneously upon exposure to air at room temperature. This process resembles the formation of the passivation layer which is common to most metals and semiconductors.

It is well documented [9] that silicon oxynitride surface exhibits a linear pH sensitivity over a broad range of values (1 - 13pH). Some authors have ascribed this sensitivity to ionization of silanol groups located in the surface plane. The linear character of the pH dependence would dictate the existence of at least thirty acid dissociation constants uniformly distributed over this pH range. The more likely explanation of the linear pH sensitivity is the existence of a hydration layer analogous to the one which forms on a glass pH electrode membrane [10].

The hydrated silicon oxynitride interface exhibits a typical non-polarized behavior [11]; it does not respond to adsorption of polyelectrolytes and is insensitive to the motion of the solution. This is again consistent with the existence of a separate phase (hydrated layer) which has the boundary potential determined by the ion exchange process only.

Finally, our previous study has shown that silicon oxynitride allows migration of charge when exposed to water [12]. The conduction properties of silicon nitride have been found to be strongly dependent on the degree of "wetness". While a dry surface would not allow charge migration for several hours, wet surface dissipates charge from electrically floating transistor gate in a matter of seconds. From the time dependence of this charge

migration the surface resistivity of $10^{16} \Omega$ square $^{-1}$ has been found for a fully encapsulated transistor chip which has been immersed in water for several days. In contrast, the surface resistivity of the chip under etching conditions at 38°C is only $10^{11} \Omega$ square $^{-1}$ as estimated from the frequency dependence of the coherence function. The lower frequency roll-off of our experimental set up does not allow us to estimate the surface resistivity of silicon oxynitride under equilibrium conditions. However, the results of this work and of the charge migration studies which were mentioned above, point to a potentially serious problem due to the cross-talk in silicon oxynitride devices which would be used under aqueous conditions. It must be pointed out, however, that silicon oxynitride is a perfect insulator, for CHEMFET applications, in direction perpendicular to the surface as has been confirmed by repeated leakage tests done throughout this study.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support for this work from the Office of Naval Research.

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LEGENDS

Figure 1. Time record of the drain current fluctuations under (a) equilibrium (buffer) and, (b) corrosion (55°C etching solution).

Figure 2. The effect of temperature on corrosion of silicon oxynitride. (a) Auto spectral density (b) coherence function.

Figure 3. The effect of mass transport on corrosion of silicon oxynitride.
(1) Low flow rate, (2) High flow rate. (a) Auto spectral density
(b) coherence function.

Figure 4. Time dependence of the current spectrum (a) and coherence (b)

Figure 5. Model of the transistor chip covered with silicon nitride under corrosion conditions. (a) Distributed impedance superimposed on channels A and B; (b) model of the impedance cell $Z_{j,k}$ with the fluctuation source $S_{j,k}$. The reference point of the cell numbers is arbitrary.

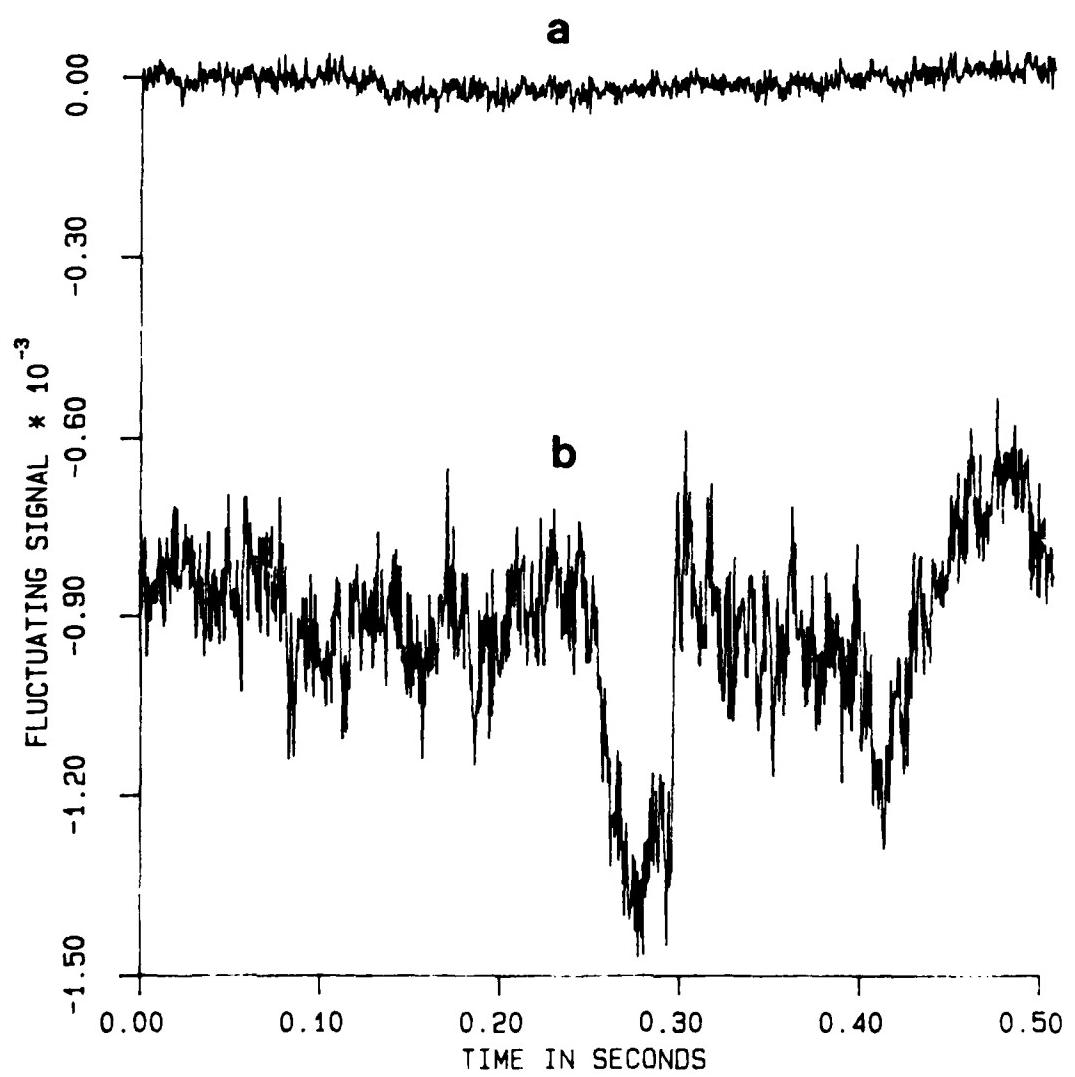


Fig. 1

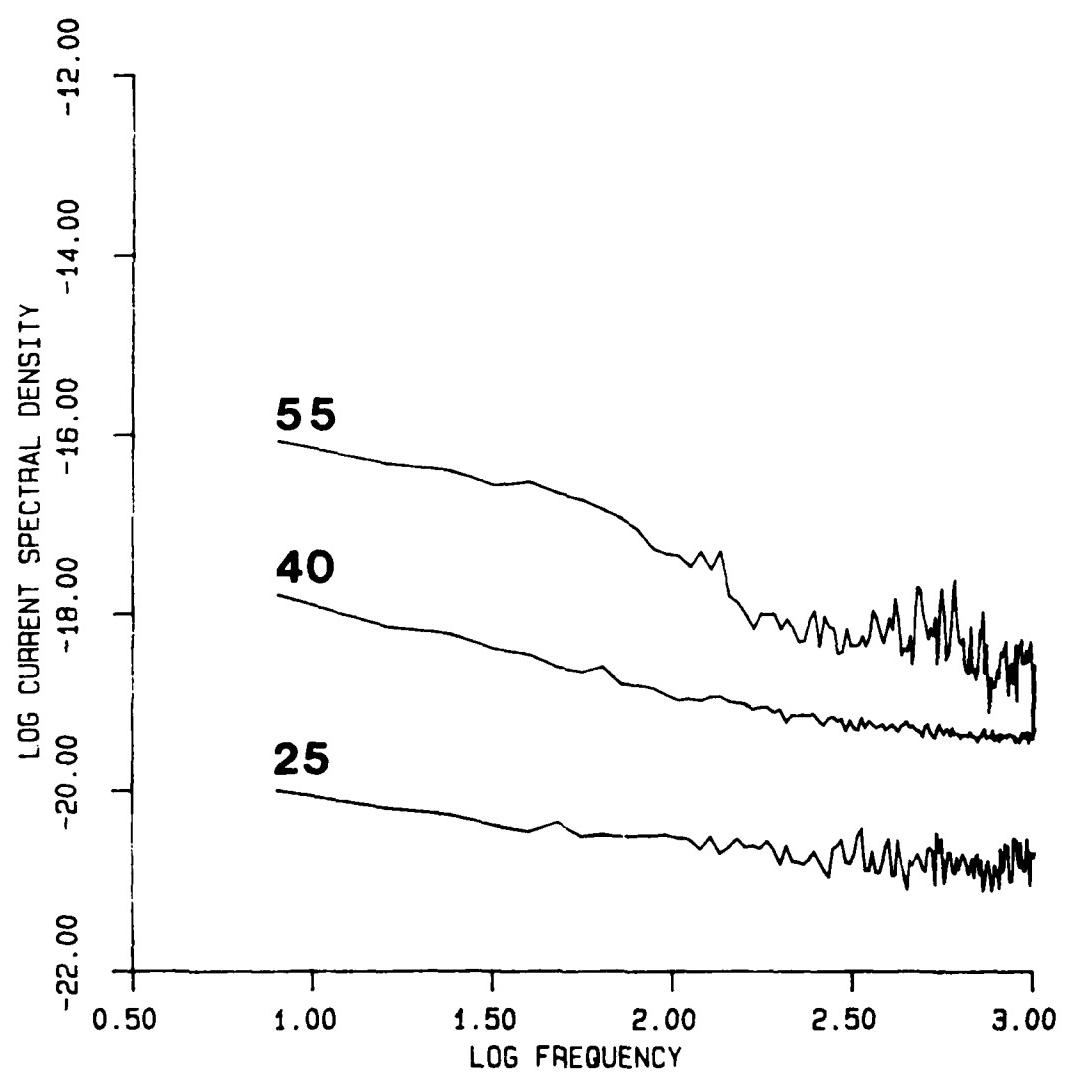


Fig. 2a

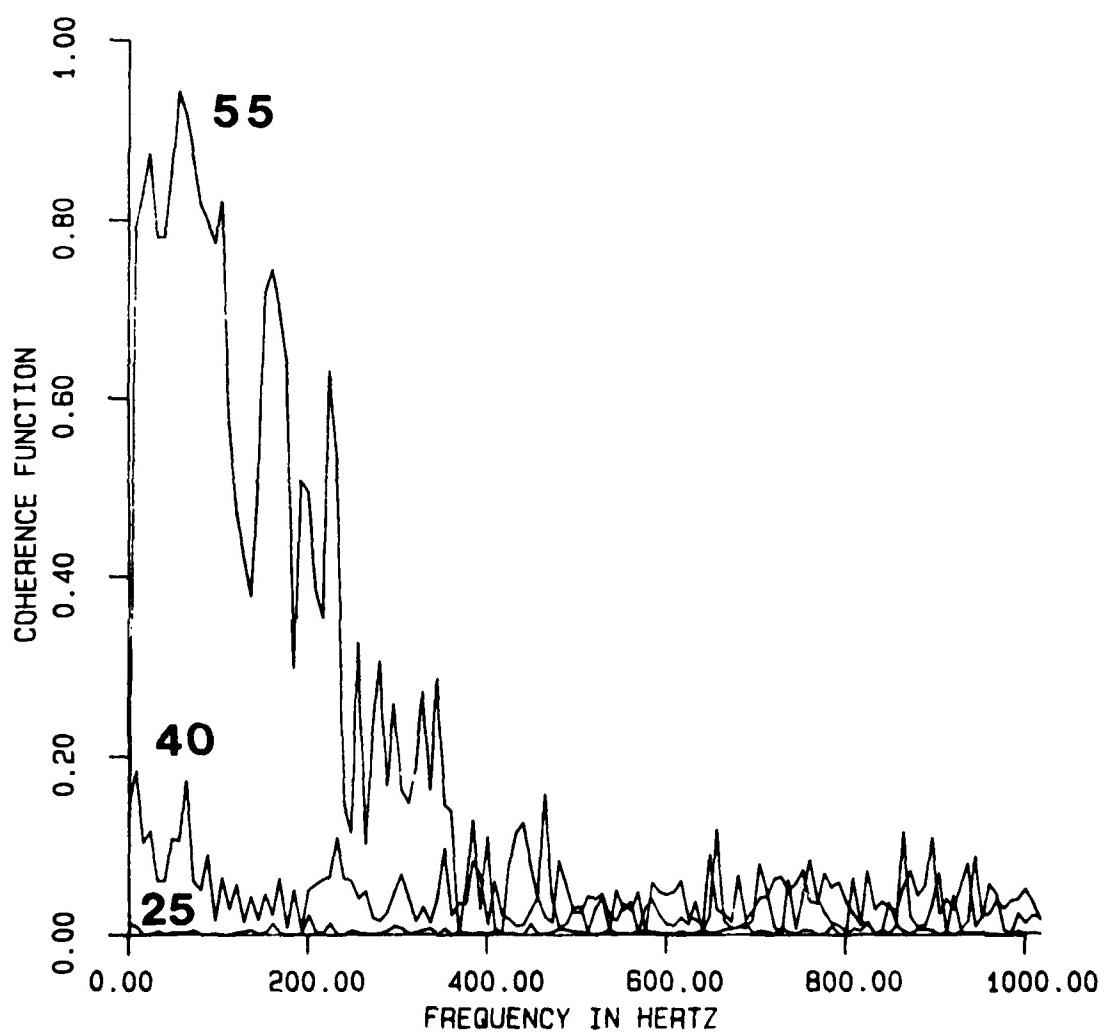


Fig. 2b

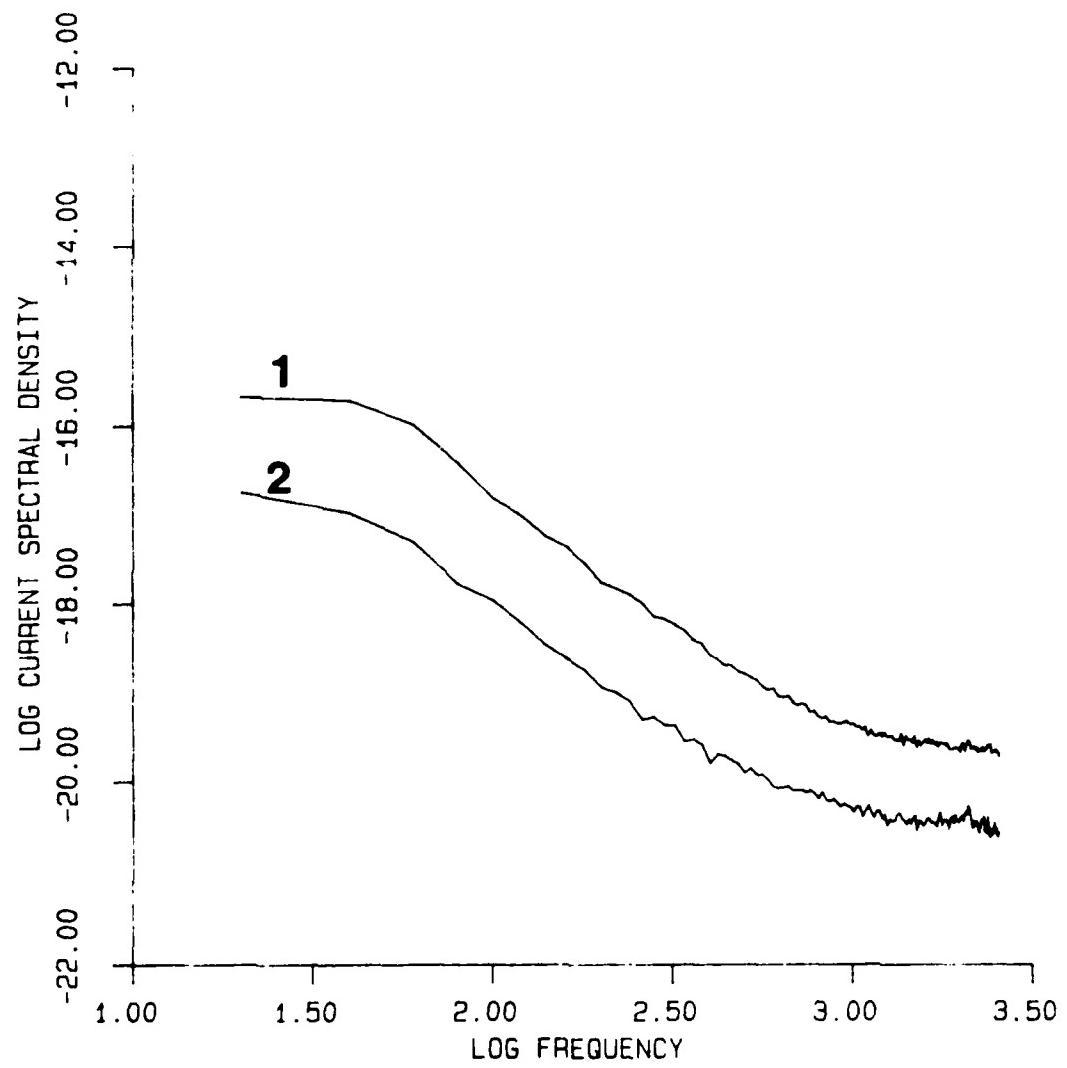


Fig. 3.2

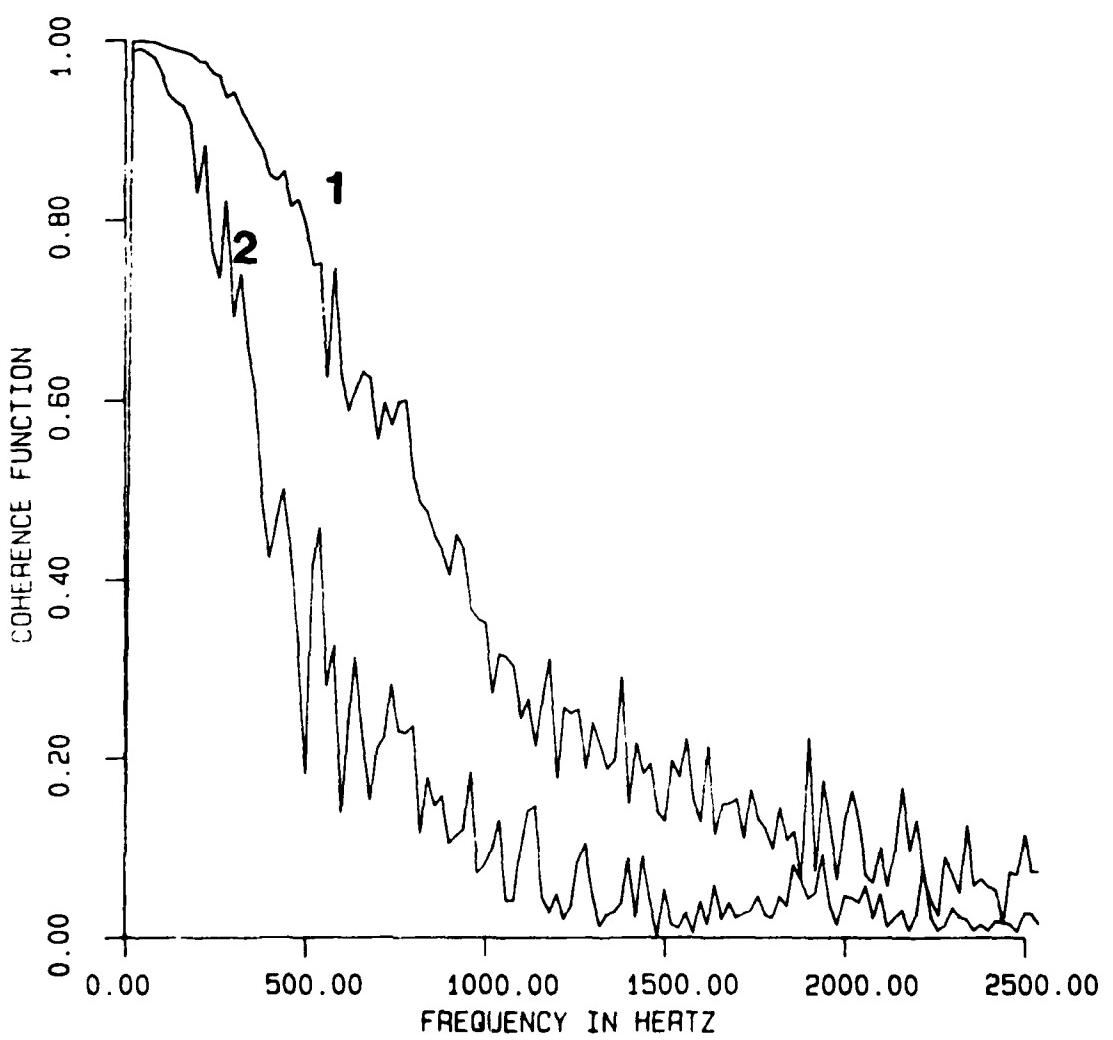
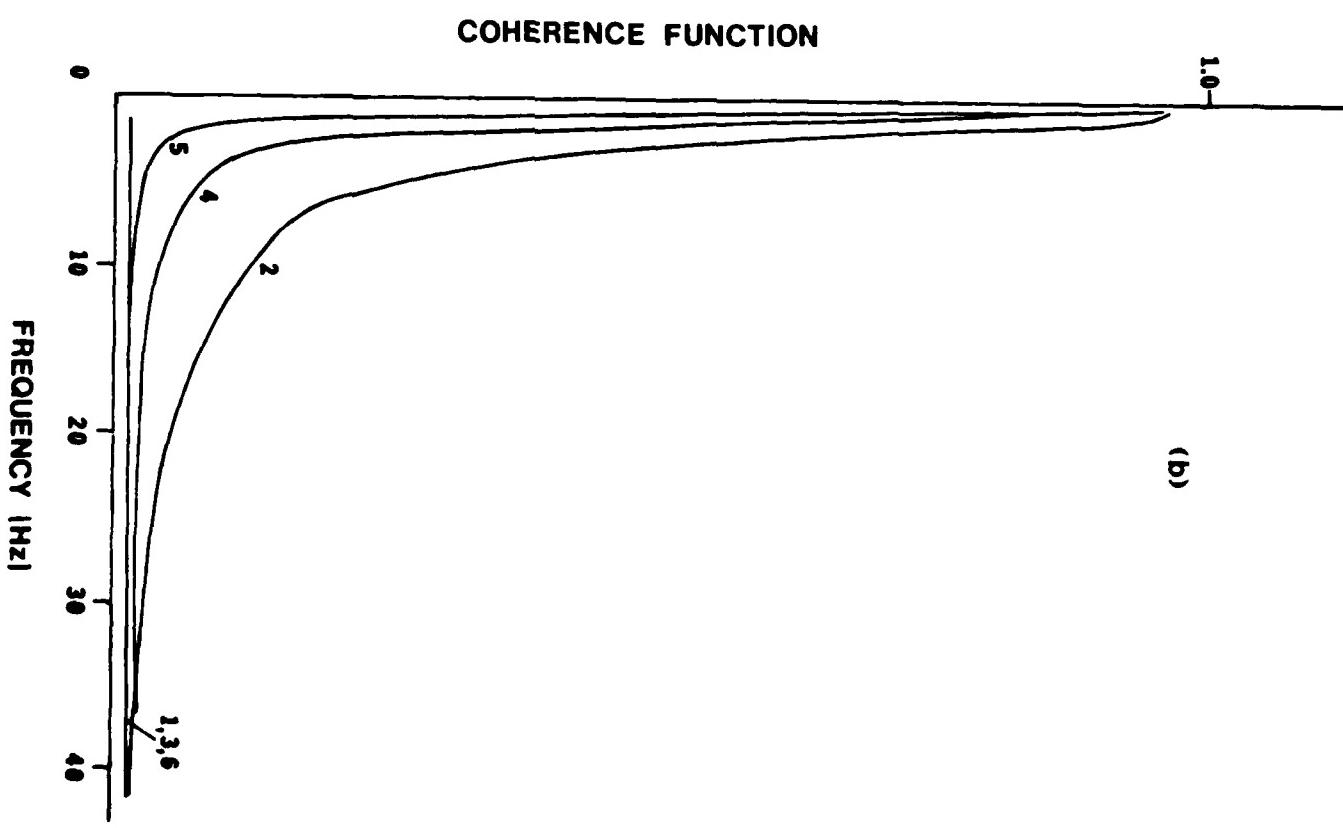
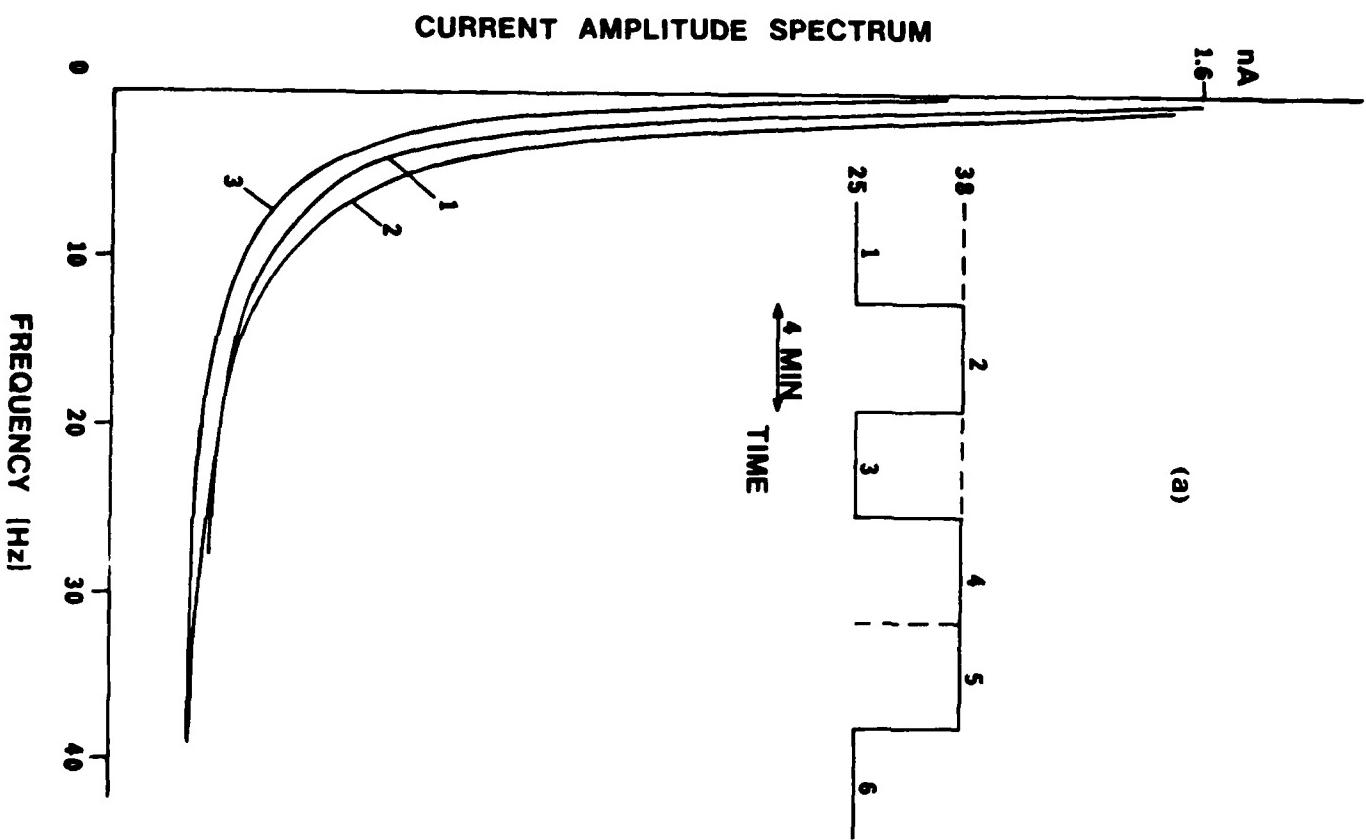


Fig. 36



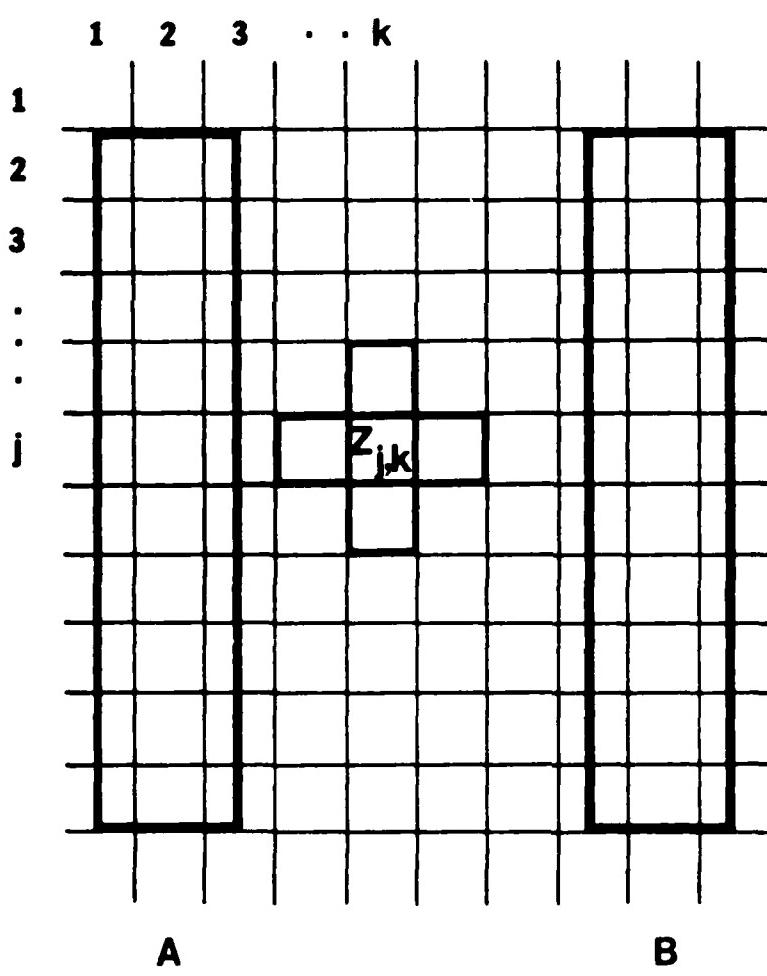


Fig 5a

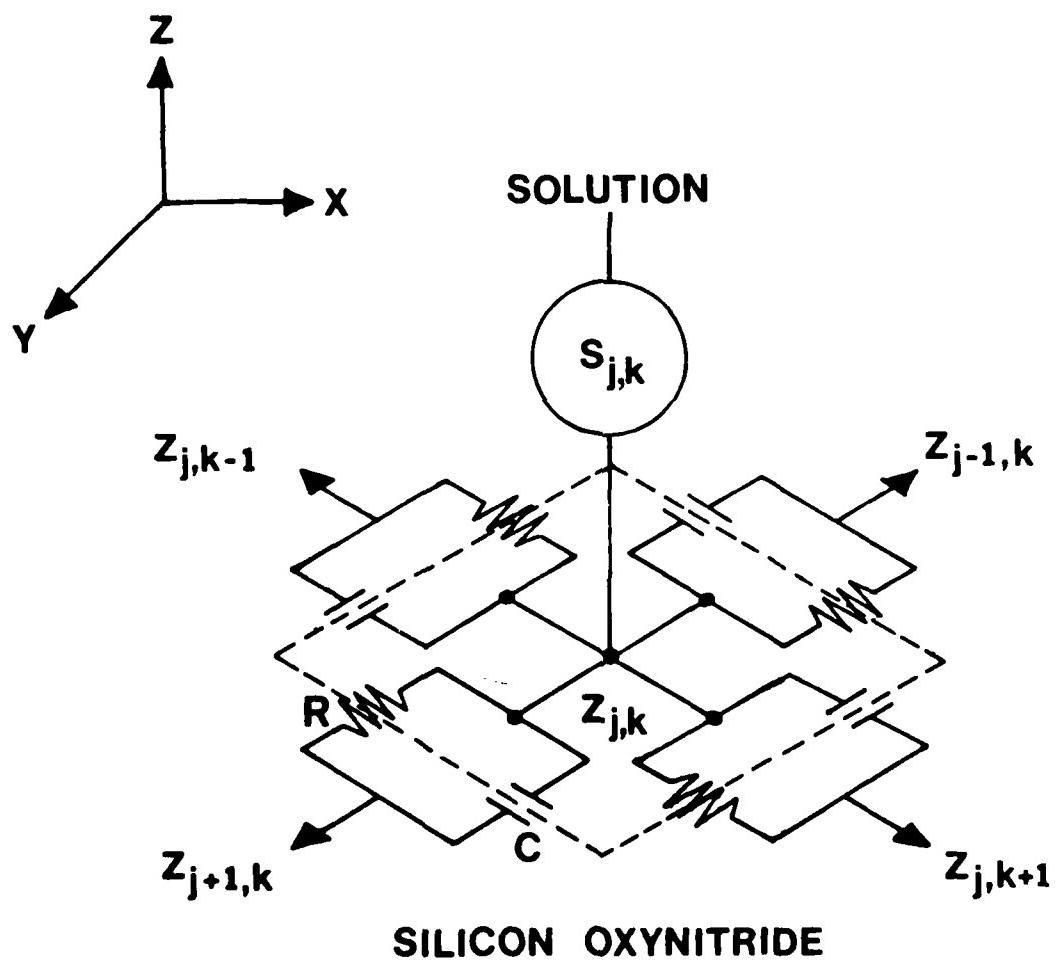


Fig. 55

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